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(54) Title: IMPROVED CATALYZED ADSORBER SYSTEM FOR TREATING INTERNAL COMBUSTION ENGINE EXHAUST GAS AND METHOD OF MAKING SAME (57) Abstract Catalyzed adsorbers for treating motor vehicle exhaust gas comprising a substrate having dispersed thereon a zeolite and an inorganic oxide washcoat, said washcoat having been impregnated with a catalytically effective amount of noble metal prior to being mixed with said zeolite and optionally with a promoter. A method of making such catalyzed adsorbers comprising treating an inorganic oxide with a noble metal reagent, mixing the product with zeolite, coating a substrate, drying and calcining.		

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IMPROVED CATALYZED ADSORBER SYSTEM FOR TREATING INTERNAL COMBUSTION ENGINE EXHAUST GAS AND METHOD OF MAKING SAME

FIELD OF THE INVENTION

5 This invention relates to catalyzed adsorbers for treating motor vehicle exhaust gas comprising a substrate having dispersed thereon a zeolite and an inorganic oxide washcoat, said washcoat having been impregnated with a catalytically effective amount of noble metals prior to being mixed or layered with said zeolite and optionally with a promoter. This invention further relates to a method of making such catalyzed adsorbers.

BACKGROUND OF THE INVENTION

10 Catalytic converters containing various catalysts have been employed for years by automobile manufacturers to meet the ever-more-stringent regulations on emissions of hydrocarbons, carbon monoxide and nitrogen oxides from internal combustion engines. The continuing evolution and tightening of these regulations has made necessary the development of systems that control emission of hydrocarbons during the period immediately after start of a cold engine and before the catalytic converter normally supplied by automobile manufacturers has been sufficiently warmed by engine exhaust gas to be effective in converting hydrocarbons (often referred to as "cold start conditions"). An attractive approach has been the incorporation in the exhaust system of an adsorbent capable of adsorbing hydrocarbons at the low exhaust gas temperatures associated with cold start (0 to 250°C) and further capable of releasing those hydrocarbons when normal exhaust system operating temperatures are achieved. Such an adsorber would normally be combined with a conventional three-way catalyst (i.e., a catalyst capable of oxidizing hydrocarbons and carbon monoxide while reducing nitrogen oxides, often referred to as a "TWC") or some other non-adsorber-containing catalyst.

25 TWC's of various types have been employed by themselves in the reduction of automobile emissions and have been effective in meeting the standards of the past. Ever-tightening regulations have, however, made necessary a more effective system for controlling emissions of unburnt hydrocarbons from internal combustion engines during cold start. The present invention provides such an improved system.

30 Various researchers have taught catalyst formulations and methods for preparation that resemble superficially the catalyzed adsorbers and method for their preparation taught here. For example, U.S. Patent N° 4,151,121 (Gladrow) teaches a catalyst for promoting the combustion of CO in the regenerators of fluid catalytic crackers to avoid afterburning. The catalyst of that patent

comprises a Group VIII element supported on an inorganic oxide and admixed with a zeolite, but also requires the presence of rhenium, chromium, manganese, or some combination thereof.

U.S. Patent N^o 5,273,945 (des Courieres *et al.*) also teaches catalysts for fluid catalytic cracking having metal supported on inorganic oxide binder or zeolite, but is indifferent to the nature of the metal employed and as to whether the metal is supported on the inorganic oxide or the zeolite.

In similar fashion, U.S. Patent N^o 3,833,499 (Egan *et al.*) teaches a catalyst for hydrocracking of hydrocarbons that employs palladium impregnated on an inorganic oxide prior to addition to a zeolite, but requires that the zeolite already be impregnated with palladium.

U.S. Patent N^o 5,278,113 (Ono *et al.*) teaches a catalyst for deodorization in room heating comprising a platinum group metal dispersed on alumina prior to being mixed with a zeolite. The catalyst of that invention is intended to effect the adsorption of odors from the environment in which it is deployed, periodically being heated to release and oxidatively decompose the odor components and thereby regenerating the catalyst.

More closely on point in the sense that the intended use is for treatment of motor vehicle engine exhaust gas, U.S. Patent N^o 5,354,720 (Leyrer *et al.*) teaches a catalyst for reducing the quantity of nitrogen oxides in lean exhaust gas that comprises a first layer of aluminum or cerium oxide impregnated with a mixture of platinum and iridium and a second layer of zeolite impregnated with copper and/or iron. The present invention is concerned with reducing the amount of hydrocarbons contained in an exhaust gas stream containing a lower oxygen concentration than those taught by the Leyrer patent.

U.S. Patent N^o 5,510,086 (Hemingway, *et al.*) teaches the use of three catalyst zones for the reduction of automobile exhaust emissions, the first of which is a conventional TWC, followed in the direction of the exhaust flow by a hydrocarbon adsorber/catalyst, which is in turn followed by another TWC. The hydrocarbon adsorber/catalyst is claimed to have a coating comprising an adhered washcoat including a zeolite and palladium. However, '086 teaches that the noble metal is to be applied to the zeolite, thereby yielding a catalytic adsorber inferior in performance to that of the instant application.

European Patent Application N^o 94309790.7 (Abe, *et al.*) teaches the use of one honeycomb monolith substrate which is coated in one region of the substrate with adsorbent for hydrocarbon, and in a completely different and distinct region of the substrate is coated with a catalyst layer active for three-way catalytic activity. The catalyst and adsorber in this example are not combined in any manner.

European Patent Application N^o 95110617.8 (Hertl, *et al.*) teaches a three brick system like

Hemingway's, with the middle adsorber brick containing a hole in the honeycomb monolith substrate to allow exhaust gas to bypass the adsorber. The invention further requires some sort of means to divert exhaust flow into or away from the adsorber brick.

SUMMARY OF THE INVENTION

This invention provides for a catalyzed adsorber that is effective and durable in treating exhaust gas from internal combustion engines, and in particular, for adsorbing hydrocarbons contained in engine exhaust gas during cold start, releasing these hydrocarbons when the engine exhaust gas has heated the adsorber to normal operating temperature and catalyzing the conversion of these hydrocarbons to carbon dioxide and water, all over one catalytic embodiment and without requiring the diversion of exhaust gas at any time during operation of the engine. Furthermore, the catalyzed adsorber of this application retains its function after exposure to severe aging by engine exhaust gas simulating 160,000 km (100,000 miles) of use in the underfloor position. The catalyzed adsorber of this invention comprises a substrate upon which has been dispersed a coating comprising an inorganic oxide that has been impregnated with a noble metal, and optionally a promoter, and an appropriate zeolite. In addition, this invention teaches a method of combining the zeolite, noble metal, inorganic oxide and optional promoter to provide optimal conversion of hydrocarbon trapped on the adsorber. This invention also includes a method of making such a catalyzed adsorber.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 compares the amount of weighted cumulative non-methane hydrocarbon (NMHC) emissions per mile vs. time from two catalyzed adsorbers of the present invention (aged 50 h.) to those from a conventional catalyst, a conventional catalyzed adsorber and a conventional non-catalyzed adsorber (all aged 50 h.).

FIG. 2 shows the rate of NMHC emissions over time during the first 200 seconds of the EPA Federal Test Procedure for Determining Emissions from Vehicles for each of the converters in FIG. 1.

FIG. 3 shows the conversion of HC and CO vs. temperature for 2.54-cm (1-inch) diameter cores taken from Pt and Pd catalyzed adsorbers of the present invention.

FIG. 4 shows the conversion of HC and NO_x vs. temperature for 2.54-cm (1-inch) diameter cores taken from Rh and Pd catalyzed adsorbers of the present invention.

FIG. 5 shows the impact of noble metal loading on the coking rates of fresh zeolite cores.

FIG. 6 shows the amount of weighted cumulative non-methane hydrocarbon (NMHC) emissions per mile vs. time from three catalyzed adsorbers of the present invention (aged 65 h.)

DETAILED DESCRIPTION OF THE INVENTION

The catalyzed adsorber of the present invention comprises a substrate which has been coated with a suitable zeolite and an inorganic oxide washcoat, the washcoat having been impregnated with a catalytically effective amount of a noble metal, and optionally admixed with a promoter, prior to being mixed with the zeolite. The noble metal and washcoat can optionally be layered on top of or underneath the zeolite layer and optional promoter, or multiple layers of zeolite and washcoat can be applied to the substrate in any combination. An important element of the present invention is the impregnation of washcoat with the noble metal prior to mixing or layering with zeolite. This prevents the noble metal or its chemical precursors from interacting with the zeolite, which would negatively impact the performance of the catalyzed adsorber after aging.

Deployment of Catalyzed Adsorber in Emissions Control System

The catalyzed adsorber ("A-brick") of the present invention may be used alone or in conjunction with a pre-adsorber catalyst ("P-brick") and/or a post-adsorber TWC ("C-brick") to reduce hydrocarbon emissions during cold start conditions of a vehicle. It is preferred that the catalyzed adsorber be placed in a location where the heat emitted by the engine will not damage the zeolite and where the temperature window is suitable for the A-brick to work well, such as in the underfloor position. If used in conjunction with a P-brick alone, the catalyzed adsorber of the present invention should be placed downstream of the P-brick; if used as part of a pre-adsorber catalyst/adsorber of the present invention/ post-adsorber catalyst ("PAC") system, the catalyzed adsorber should be placed downstream of the P-brick and upstream of the C-brick. The P-brick and C-brick may be any noble metal catalyst formulation which may be used as a TWC, such as, but not limited to, Pd-only, Rh-only, Pd/Rh, Pt/Rh, or Pt/Pd/Rh. The P-brick preferably will be designed to provide rapid light-off and conversion of hydrocarbons.

If used alone, or in conjunction with only a P-brick, the catalyzed adsorber should be sized so that the HC mass emissions during cold start conditions (i.e., before the P-brick lights off) are no more than 80 % of the desired emission or standard. If used as part of a PAC system, the catalyzed adsorber should be sized so that its volume is between about one quarter of to about twice the volume of the C-brick. The size of the C-brick is determined by methods known to those skilled in the art.

Substrate

The substrate should be inert in the sense that it does not react with the coating or with the exhaust gas to which it is exposed during engine operation. The substrate may be any of the shapes employed by those skilled in the art such as extrudates, spheres, beads, tablets, ceramic foams, and the like, but monoliths, either metallic or ceramic, are preferred.

5 If a monolith is employed as the substrate, it should be sized and shaped so that it fits within whatever vessel is employed as a container and leaves no gaps between the vessel interior wall and the outside surface of the monolith which might result in blow-by of the exhaust gas past the monolith (i.e., bypassing of the catalyzed adsorber). Ceramic monoliths, if employed, should be provided with a mat-mount between the exterior surface of the monolith and the vessel wall, as is customary in the
10 industry, to cushion vibration during engine operation and to prevent blow-by of the engine exhaust gas past the catalyst. Metallic monoliths should be attached to the vessel wall, as is customary.

Monolith coating loads will depend on the engine and vehicle characteristics along with the zeolite adsorption capacity and noble metal activity, but should be coated with between about 0.061 gram of zeolite plus washcoat and about 0.366 grams of zeolite plus washcoat per cm^3 (between 1
15 and 6 gram/in^3) of substrate, preferably between 0.183 and 0.305 grams of zeolite plus washcoat per cm^3 (between 3 and 5 gram/in^3) of substrate.

Zeolite

Several different zeolites may be advantageously used in the catalyzed adsorbers of the present invention. To a great extent, the choice of zeolite is dictated by the characteristics of the
20 exhaust gas for which treatment is intended. In all cases, the zeolite by itself must be capable of retaining adsorption capacity for hydrocarbons when exposed to the same operating conditions as a conventional TWC located in an underfloor position for 160,000 km (100,000 miles).

In all applications, however, the zeolite chosen must have the following characteristics:

- 25 a) It must be capable of adsorbing hydrocarbon preferentially over water in the range of operating temperatures which it will encounter in its application; that is, from near ambient temperature to normal operating temperature, and when exposed to exhaust gas compositions, which generally include about 10 vol.% steam.
- 30 b) It should have a high heat of adsorption for all the hydrocarbon molecules contained in the exhaust gas to be treated. The heat of adsorption should be at least about 4.5 kcal per gram-mol. of hydrocarbon adsorbed at 150°C , and preferably should be at least about 9.5 kcal per gram-mol. of hydrocarbon adsorbed at 150°C .
- c) It must be stable when exposed to exhaust gas normal operating conditions and

should be capable of withstanding the accelerated aging conditions employed by automobile manufacturers to test emission control systems durability. Preferably, the zeolite chosen should be capable of experiencing little damage to its hydrocarbon storage and release properties from exposure to steam at temperatures up to about 850°C and should not be subject to crystal collapse at temperatures below 980°C.

- d) It must be, after mixture or layering with the inorganic oxide binder chosen for the desired application, suitable for application on a monolithic substrate, yielding a tough, adherent coating not subject to dusting, flaking, or spalling.
- e) It must be able to sustain mild milling required to insure coatability prior to admixing or layering with the noble-metal-treated inorganic oxide washcoat.

The preferred zeolite to be used in the manufacture of a catalyzed adsorber of the present invention is a faujisite having a Si/Al ratio between about 3.0 and about 10 and a Na content less than about 0.1 wt.%. The low sodium content is achieved by ion exchanging the zeolite with ammonium cation or other metal cations by means well known in the art. An example of the preferred zeolite is LZ-210 manufactured by UOP, Inc. which is described in U.S. Patent No. 4,711,770, incorporated herein by reference.

Inorganic Oxide Washcoat

The inorganic oxide washcoat serves two functions simultaneously. First, the washcoat serves as a noble metal support. Second, when mixed with zeolite before application to a substrate, the washcoat improves the adhesion of the mixture as a whole. The catalyzed adsorber must contain at least one inorganic oxide washcoat in addition to a noble metal and a zeolite.

Washcoats appropriate for combining or layering with the useful zeolites herein include inorganic oxides such as alumina, silica, alumina-silicates, titania, magnesia, zirconia, beryllia, and mixtures thereof, with alumina, titania, and zirconia being preferred. Small amounts, up to about 30 wt. % of a rare earth oxide, such as ceria, lanthana, zirconia, or mixtures thereof may be added to the washcoat to act as a promoter for the noble metal employed. In addition, a small amount of a stabilizer, such as barium oxide or barium sulfate may be added. Optionally, the washcoat may consist of a stabilized ceria, such as ceria-zirconia, entirely or in part.

The relative proportions of zeolite and inorganic oxide washcoat in the coating to be applied to the substrate may vary widely with the zeolite content ranging from about 40 to about 80 wt. %, preferably in the range of about 70 to about 80 wt. % for catalyzed adsorbers made by mixing the zeolite and washcoat together before application to the substrate and preferably in the range of about

40 to about 60 wt. % for catalyzed adsorbers made by layering the zeolite and the washcoat.

Noble Metal

The noble metals of choice for this invention are palladium, platinum, rhodium, and mixtures and alloys of rhodium with either palladium or platinum, but any Group VIII metal, or mixture thereof, may be used. The preferred noble metal is palladium due to its relatively low lightoff temperature (i.e., the catalyzed adsorber temperature that results in conversion of 50 % of the hydrocarbons contained in the exhaust gas) and relatively low cost.

Recommended noble metal loading is a function of the metal chosen. For Pd, the loading should be between about 1,765 and about 8,830 grams of Pd per m³ (between about 50 and about 250 grams of Pd per ft.³) of monolithic substrate, and preferably between about 3,180 and about 7,060 grams of Pd per m³ (between about 90 and about 200 grams of Pd per ft.³) of monolithic substrate. For Pt, the loading is typically, but not limited to, between about 350 and about 2,470 grams of Pt per m³ (between about 10 and about 70 grams of Pt per ft.³) of monolithic substrate, and preferably between about 1,410 and about 2,470 grams of Pt per m³ (between about 40 and about 70 grams of Pt per ft.³) of monolithic substrate. For Rh, the loading is typically, but not limited to, between about 175 and about 1,060 grams of Rh per m³ (between about 5 and about 30 grams of Rh per ft.³) of monolithic substrate, and preferably between about 530 and about 1,060 grams of Rh per m³ (between about 15 and about 30 grams of Rh per ft.³) of monolithic substrate.

Preparation of Catalyzed Adsorber

As illustrated by FIG. 1, the manner in which catalyzed adsorbers are made has a large impact on fresh and particularly aged performance. An important consideration in preparing a catalyzed adsorber of the present invention is the requirement that impregnation or dispersion of the noble metal be predominately on the inorganic oxide washcoat material in the final catalyzed adsorber formulation. The most convenient method for accomplishing this is through the application of a suitable noble metal reagent directly to the washcoat in the absence of zeolite. Other methods that result in the noble metal being dispersed predominately on the washcoat and not on the zeolite are known and may be employed as a matter of choice. Separating the noble metal from the zeolite helps eliminate interactions between highly acidic and reactive noble metal solutions and the zeolite material. This separation thus improves the durability of the zeolite as well as preserving noble metal dispersion, and it limits potential poisoning of active noble metal sites by the debris or mobile components from the zeolite during high temperature aging. This action also improves the durability

of the noble metal thereby improving aged light-off and steady state conversion of hydrocarbons, carbon monoxide, and nitrogen oxides in the engine exhaust with which the catalyzed adsorber is contacted. Having the noble metal in close proximity to the zeolite, on the other hand, is important to prevent coking of the zeolite and to enhance combustion of hydrocarbon as it desorbs from the zeolite.

The preferred method of preparation, then, calls for a wet impregnation of noble metal reagent on an inorganic oxide washcoat, sufficient to provide the desired loading of noble metal on the final catalyzed adsorber part. Any noble metal reagent known to those skilled in the art may be employed. For instance, but not by way of limitation, a 7-8 wt. % aqueous solution of palladium nitrate is impregnated on the washcoat of a catalyzed adsorber employing Pd as the noble metal. A similar solution of platinum nitrate would be preferred for deposition of Pt. The impregnated washcoat is dried for at least 24 hours to allow precious metal to fully chemisorb on the inorganic oxide washcoat and then calcined at a temperature equal to or less than 250° C for 2 hours. The calcined, impregnated washcoat is then slurried in water and the pH is adjusted to between about 3.1 and about 3.9 by the addition of an organic acid, preferably acetic acid, and the mixture is milled for about 20 minutes to one hour to provide good coatability. Acids such as nitric acid should be avoided due to their tendency to interact adversely with the zeolite. At the same time, additional promoters or additives can be added directly to the slurry, if desired. The washcoat suspension is then combined with an aqueous suspension of zeolite and the whole is milled briefly, as required for good coating.

After stirring the combined mixture for at least an hour, the resulting slurry is applied to the substrate by any of the methods known to those skilled in the art, including, without limitation, immersion of the substrate in the slurry or spraying of the slurry onto the substrate. Following application of the slurry to the substrate, the coated substrate is dried and then calcined at a temperature of between about 400°C and about 550°C for 2 to 4 hours.

Another method of preparation calls for a wet impregnation of noble metal reagent on an inorganic oxide washcoat, sufficient to provide the desired loading of noble metal on the final catalyzed adsorber part. Any noble metal reagent known to those skilled in the art may be employed. As in the method above, a 7-8 wt% aqueous solution of palladium nitrate is impregnated on the washcoat of a catalyzed adsorber employing Pd as the noble metal, and a similar solution of platinum nitrate would be preferred for deposition of Pt. The impregnated washcoat is dried for at least 24 hours and then calcined at a temperature equal to or less than 250° C for 2 hours. The calcined, impregnated washcoat is then slurried in water and its pH is adjusted to between about 3.1 and about 3.9 by the addition of an organic acid, preferably acetic acid, and the suspension is milled for about

one hour to provide good coatability. An aqueous suspension of zeolite is prepared separately and then milled briefly, not more than 10 minutes, as required for good coating.

In the first coating step, the zeolite suspension or the impregnated washcoat suspension is then applied to the substrate by any of the methods known to those skilled in the art, including immersion of the substrate in the suspension or spraying of the suspension onto the substrate. The coated substrate is dried and then calcined at a temperature between 400°C and 550°C for 2 to 4 hours. The process is repeated with the suspension which was not coated in the first coating step. Following application of the second slurry to the substrate, the layered and coated substrate is dried and then calcined at a temperature of between about 400°C and about 550°C for 2 to 4 hours. The process may be repeated again as many times as desired if a multi-layered washcoat is required.

EXAMPLE 1

This example describes the preparation of a catalyzed adsorber of the present invention.

An aqueous Pd nitrate solution was uniformly impregnated onto alumina powder in an amount such that the resulting impregnated powder contained 132.2 grams of Pd per kg of alumina. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C. An aqueous suspension of the impregnated powder was then prepared and the pH was measured. If needed, sufficient acetic acid to lower the pH to about 3.5 was then added and then the suspension was milled to obtain a particle size between 7 and 15 microns. Next, a sufficient quantity of a milled suspension of UOP CSX-455 zeolite (milled just enough to break up the lumps in suspension to allow good coatability) was added to the suspension of milled impregnated powder to form a slurry in which the ratio of zeolite to alumina was about 3:1. The mixture was then stirred for 3 hours, following which it was coated onto ceramic monoliths, then the coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours. One finished catalyzed adsorber (A-brick) was installed in a converter between a 7,060 g Pd per m³ (200 g Pd per ft.³) of substrate P-brick and a 5,300 g Pd/Rh in a 15/1 ratio per m³ (150 g Pd/Rh per ft.³) of substrate C-brick to form a PAC system suitable for performance evaluation.

EXAMPLE 2

This example describes the preparation of a catalyzed adsorber of the prior art.

An aqueous suspension of alumina powder was prepared and sufficient Pd nitrate was added to yield an aqueous suspension of alumina powder having 165.4 grams of Pd per kg of alumina. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a

particle size between 7 and 15 microns. Then a sufficient quantity of a milled suspension of UOP CSX-455 zeolite was added to the washcoat suspension to form a slurry in which the ratio of zeolite to washcoat was about 3:1. The mixture was then stirred and coated onto monolith substrates as in Example 1. PAC systems were made in the same manner as Example 1, except the adsorber brick was made by the method of this example.

EXAMPLE 3

This example describes an alternative preparation of a catalyzed adsorber of the present invention.

An aqueous Pd nitrate solution was uniformly impregnated onto a mixture of alumina powder and Zr-rich mixed oxide $\text{ZrO}_2/\text{CeO}_2$ powder such that the weight ratio of the mixed oxide and the alumina was 1.0, and such that the resulting impregnated powder contained 132.2 grams of Pd per kg of alumina/mixed oxide powder. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C . An aqueous suspension of the impregnated powder was then prepared and the pH was measured. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a particle size between 7 and 15 microns. Next, a sufficient quantity of a milled suspension of UOP CSX-455 zeolite was added to the suspension of impregnated powder to form a slurry in which the ratio of zeolite to alumina was about 3:1. The mixture was then stirred for 3 hours, following which it was coated onto ceramic monoliths, then the coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours. One finished catalyzed adsorber (A-brick) was installed in a converter between a $7,060 \text{ g Pd per m}^3$ ($200 \text{ g Pd per ft.}^3$) of substrate P-brick and a $5,300 \text{ g Pd/Rh}$ in a 15/1 ratio per m^3 ($150 \text{ g Pd/Rh per ft.}^3$) of substrate C-brick to form a PAC system suitable for performance evaluation.

EXAMPLE 4

This example describes an alternate preparation of a catalyzed adsorber of the present invention.

An aqueous suspension of UOP CSX zeolite powder and alumina, in which the ratio of zeolite to alumina was about 4 to 1, was prepared and milled for 10 minutes. The suspension was then stirred for three hours, following which it was coated onto ceramic monoliths. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours.

An aqueous Pd nitrate solution was uniformly impregnated onto a mixture of alumina powder and stabilized Zr powder (83.6 wt. % ZrO_2 , 14.5 wt. % CeO_2 , and 1.9 wt. % La_2O_3) such that the

weight ratio of the stabilized Zr to the alumina was 2.0, and such that the resulting impregnated powder contained 132.2 grams of Pd per kg of alumina/mixed oxide powder. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C. An aqueous suspension of the impregnated powder was then prepared and the pH was measured. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a particle size between 7 and 15 microns. The mixture was then stirred for three hours, following which it was coated onto the ceramic monoliths which were previously coated with zeolite. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours. One finished catalyzed adsorber made by the method of this example was installed in a converter in a PAC configuration as in Example 1.

EXAMPLE 5

This example describes the preparation of a non-catalyzed adsorber sample.

An aqueous suspension of UOP CSX zeolite powder and alumina, in which the ratio of zeolite to alumina was about 4 to 1, was prepared and milled for 10 minutes. The suspension was then stirred for three hours, following which it was coated onto ceramic monoliths. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours.

EXAMPLE 6

This example describes an alternate preparation of a catalyzed adsorber of the present invention.

An aqueous Pt nitrate solution was uniformly impregnated onto alumina powder in an amount such that the resulting impregnated powder contained 46.3 grams of Pt per kg of alumina. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C. An aqueous suspension of the impregnated powder was then prepared and the pH was measured. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a particle size between 7 and 15 microns. Next, a sufficient quantity of a milled suspension of UOP CSX-455 zeolite was added to the suspension of impregnated powder to form a slurry in which the ratio of zeolite to alumina was about 3 to 1. The mixture was then stirred for three hours, following which it was coated onto ceramic monoliths. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours.

EXAMPLE 7

This example describes an alternate preparation of a catalyzed adsorber of the present invention.

An aqueous Rh nitrate solution was uniformly impregnated onto a mixture of alumina powder and stabilized Zr powder such that the weight ratio of the stabilized Zr powder and the alumina was 1.0, and such that the resulting impregnated powder contained 19.8 grams of Rh per kg of alumina/mixed oxide powder. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C. An aqueous suspension of the impregnated powder was then prepared and the pH was measured. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a particle size between 7 and 15 microns. Next, a sufficient quantity of a milled suspension of UOP CSX-455 zeolite was added to the suspension of impregnated powder to form a slurry in which the ratio of zeolite to alumina was about 3 to 1. The mixture was then stirred for three hours, following which it was coated onto ceramic monoliths. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours.

EXAMPLE 8

This example describes an alternate preparation of a catalyzed adsorber of the present invention.

An aqueous water soluble Pd carboxylic acid solution was uniformly impregnated onto alumina powder in an amount such that the resulting impregnated powder contained 59.5 grams of Pd per kg of alumina. The powder was dried for 24 hours in room temperature air, and then calcined for 2 hours at 250°C. An aqueous suspension of the impregnated powder was then prepared and the pH was measured. The pH of the suspension was lowered to about 3.5 with acetic acid and then was milled to obtain a particle size between 7 and 15 microns. Next, a sufficient quantity of a milled suspension of UOP CSX-455 zeolite (milled just enough to break up the lumps in suspension to allow good coatability) was added to the suspension of milled impregnated powder to form a slurry in which the ratio of zeolite to alumina was about 3 to 1. The mixture was then stirred for three hours, following which it was coated onto ceramic monoliths. The coated monoliths were dried and then calcined at a temperature of about 550°C for 2 hours. One finished catalyzed adsorber (A-brick) was installed in a converter between a 7,060 g Pd per m³ (200 g Pd per ft.³) of substrate P-brick and a 5,300 g Pd/Rh in a 15/1 ratio per m³ (150 g Pd/Rh per ft.³) of substrate C-brick to form a PAC system suitable for performance evaluation.

EXAMPLE 9
(Comparative)

An important element of the present invention is the impregnation of washcoat with the noble metal prior to mixing or layering with zeolite. This prevents the noble metal or its chemical precursors from interacting with the zeolite, which will negatively impact the light-off of the catalyzed adsorber after aging. Catalyzed HC Adsorbers made using the methods of Examples 1 and 2 were aged in an oven for 2 hours at 800°C and then an additional 2 hours at 900°C in 10% water and nitrogen. The aged HC adsorbers were placed in converters, which were then installed one at a time on a 1995 Oldsmobile with a 3.8L engine, and the vehicle's emissions with each converter were evaluated using the EPA's Federal Test Procedure for Determination of Vehicle Emissions. Table 1 shows a comparison of the light-off performance on the vehicle of Examples 1 and 2. A shorter time to light-off or a lower light-off temperature will result in lower emissions.

TABLE 1. Vehicle Light-Off Performance of Catalyzed Adsorbers

Catalyzed Adsorber	Time from start of FTP to light-off, seconds	Light-off Temperature, °C
Example 1 - Current Invention	70	310
Example 2 - Prior Art	95	390

*Light-off Temperature is the temperature at which 50% of the incoming HC has been converted.

EXAMPLE 10
(Comparative)

Catalyzed HC Adsorbers made using the methods of Examples 1, 2, 5, and 8 were combined with Pd-only front bricks and conventional TWC rear bricks in PAC systems, and then installed in 2.7 L converters. A conventional non-adsorber catalyst, with the same noble metal loadings as in Example 1, was installed in an additional converter. This sample served to illustrate what could be converted in the absence of HC adsorption. All of the converters were aged using a high temperature aging cycle on an engine dynamometer to simulate 100,000 miles of use on a vehicle. (The accelerated aging constituted 50 hours on an engine dynamometer exposing the adsorber to bed temperatures up to 910°C.) The aged converters were installed one at a time on a 1995 Oldsmobile with a 3.8 L engine, and the vehicle's emissions with each converter were evaluated using the EPA's

Federal Test Procedure for Determination of Vehicle Emissions. The test results are shown in Figure 1 as weighted accumulated HC emissions per mile over time, and indicate that the systems which used HC Adsorbers of the present invention were able to meet the California Low Emission Vehicle Standard for passenger cars of 0.04688 grams per km (0.075 grams per mile). The converters which
 5 utilized adsorbers which were not of the present invention, or which did not use an adsorber, were unable to convert enough of the vehicle's exhaust to allow it to achieve the Low Emission Vehicle Standard. Results also indicate that the use of Pd precursor in Example 8 provides equivalent performance to Pd nitrate at a lower loading.

Additional results are shown in Figure 2, which shows the rate of HC emission in grams HC
 10 per second provided by each converter over the first 100 seconds of the emission test. This figure clearly shows the benefit of an adsorber during the first 40 seconds of vehicle operation, since the emissions from the adsorber containing converter systems during this time are significantly less than those from the non-adsorber system. Furthermore, the HC emissions from the converters which contain adsorbers of the present invention (Examples 1 and 8) are less than those which contain
 15 adsorbers which are of the prior art (Examples 2 and 5) during this same 40 second time period.

Table 2 shows the results for HC, CO and NO_x tailpipe emissions for the PAC converters tested above. It shows that CO and NO_x conversions over the three brick catalyzed adsorber systems of the present invention are equivalent to conventional three-way catalysts.

TABLE 2

Effect of Adsorber Type on Vehicle Tailpipe Emissions from PAC Converter Systems.

Adsorber Type	NMHC		CO		NO _x	
	g/km	(g/mile)	g/km	(g/mile)	g/km	(g/mile)
Example 1 (present invention)	.039	(.062)	.44	(.71)	.07	(.11)
Example 2 (prior art)	.054	(.087)	.45	(.72)	.07	(.12)
Example 5 (prior art)	.063	(.101)	.76	(1.22)	.11	(.18)
Example 8 (present invention)	.040	(.065)	.49	(.79)	.06	(.10)
Non-Adsorber(=Conventional Three-way catalyst)	.057	(.092)	.44	(.71)	.09	(.15)

Example 11
(Comparative)

Catalyzed HC Adsorbers were made using the methods of Examples 1, 6 and 7, and then a one inch diameter core was cut from each finished monolith part. The cores were aged in a quartz tube furnace for 2 hours at 800°C and 2 hours at 900°C in an atmosphere of nitrogen and 10% water. After aging, the cores were tested in a laboratory reactor using a synthetic gas mixture which
 35 was representative of an automobile running at a stoichiometric air/fuel ratio. The inlet temperature

to the cores was ramped from 25°C to 350°C at 10°C/minute as the synthetic gas mixture was passed over the cores, and the exhaust from each core was analyzed. The percent conversion of HC and CO vs. temperature for the samples from Example 1 and Example 6 is shown in Figure 3, while the percent conversion of HC and NO_x vs. temperature from Example 1 and Example 7 is shown in Figure 4. Both figures show a characteristic adsorption phase, followed by catalyst light-off for all the samples tested. The lab results show that Pt or Rh is a suitable substitute for Pd as the active catalytic ingredient of the adsorbers of the present invention. The Rh sample appears to provide better NO_x than the Pd sample, while the Pt sample provides better CO conversion.

EXAMPLE 12 (Comparative)

Catalyzed HC Adsorbers were made using the methods of Examples 1 and 5, then a one inch diameter core was cut from each finished monolith part. A conventional Pd catalyst was made separately and a core was also cut from it. The cores were tested in a laboratory reactor using a synthetic gas mixture which was representative of an automobile running at a rich air/fuel ratio. As the synthetic gas was passed over each core, the temperature was cycled between 50 and 250°C at 7°C/minute in such a manner as to promote coking on the zeolite. Figure 5 is a plot of the grams of HC adsorbed during each cycle of the test versus the cycle number. Results from the figure indicate that a 5.08 cm (2 inch) length core made using the method of Example 5 (non-catalyzed adsorber), when used by itself, starts with good adsorption capacity during the first test cycle but as the number of test cycles increase, the adsorption capacity decreases significantly. Cutting the Example 5 core in half and putting a conventional catalyst upstream of it solves the problem: for this case there is no decline in adsorption with increasing cycle number. The same effect can be achieved by using a catalyzed adsorber of the present invention. Therefore, the curve for Example 1 in Figure 5 also indicates no decline in adsorption capacity with increasing test cycle. Using a catalyzed adsorber of the present invention eliminates the need for placing a conventional three-way catalyst upstream of the adsorber.

EXAMPLE 13 (Comparative)

Catalyzed HC Adsorbers made using the methods of Examples 1, 3, and 4 were combined with Pd/Rh front bricks in Pre-adsorber catalyst /Adsorber of the present invention (PA) systems, and then installed in 2.7 L converters. All of the converters were aged using a European severe temperature aging cycle on an engine dynamometer to simulate 160,000 km (100,000 miles) of use

on a vehicle. (The accelerated aging constituted 65 hours on an engine dynamometer exposing the adsorber to bed temperatures up to 970°C.) The aged converters were installed one at a time on a 1996 Mercedes Benz car with a 2.0 L engine, and the vehicle's emissions with each converter were evaluated using the EPA's Federal Test Procedure ("FTP test") for determination of vehicle emissions. The test results are shown in Figure 6 as weighted accumulated HC emissions per mile over time, and indicate that for the European aging cycle, the layered HC adsorber made by the method of Example 4 has an advantage over the adsorbers made by other manifestations of the present invention such as those of Example 1 or Example 3, when utilized in a two brick system.

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CLAIMS

We claim:

1. A catalyzed adsorber for treating motor vehicle exhaust gas comprising a substrate coated
5 with a zeolite and an inorganic-oxide washcoat, said inorganic-oxide washcoat having been impregnated with a catalytically effective amount of noble metal prior to being mixed with said zeolite, and optionally with a promoter.
2. The catalyzed adsorber of Claim 1 wherein the substrate is selected from the group consisting
10 of ceramic monoliths, ceramic foams, and metallic monoliths.
3. The catalyzed adsorber of Claim 1 wherein the inorganic oxide washcoat is selected from the group consisting of alumina, silica, alumina-silicates, titania, magnesia, zirconia and ceria, and mixtures thereof.
15
4. The catalyzed adsorber of Claim 1 wherein the noble metal is selected from the group consisting of Pt, Pd, Rh, and mixtures and alloys thereof.
5. The catalyzed adsorber of Claim 1 wherein the optional promoter is selected from the group
20 consisting of lanthana, ceria, zirconia, and mixtures thereof.
6. The catalyzed adsorber of Claim 5 wherein the adsorber contains a promoter stabilized with a stabilizer selected from the group consisting of barium oxide and barium sulfate.
- 25 7. The catalyzed adsorber of Claim 1 wherein the zeolite is a faujisite having a Si/Al ratio of about 10 and having a Na content below about 0.1 wt.%.
8. A catalyzed adsorber for treating motor vehicle exhaust gas comprising a substrate having dispersed thereon a zeolite layer and an inorganic-oxide-washcoat layer, said washcoat layer
30 having been impregnated with a catalytically effective amount of noble metal and optionally with a promoter, wherein one of said layers is dispersed on the substrate and then the other layer is dispersed on the layer first dispersed.

9. An exhaust emissions control system comprising at least one three-way catalyst and the catalyzed adsorber of Claim 1.
10. An exhaust emissions control system comprising at least one three-way catalyst and the catalyzed adsorber of Claim 8.
11. A process for making the catalyzed adsorber of Claim 1 comprising:
- a) impregnating a catalytically effective amount of noble metal reagent on an inorganic oxide washcoat, thereby making a noble-metal-impregnated washcoat;
 - b) drying the noble-metal-impregnated washcoat for at least 24 hours;
 - c) optionally calcining the washcoat at a temperature above about 250°C for between about 1 and about 2 hours;
 - d) preparing an aqueous suspension of the washcoat;
 - e) adjusting the pH of the suspension to between about 3.1 and about 3.9 by the addition of an organic acid;
 - f) milling the suspension for about 1 hour;
 - g) preparing an aqueous suspension of zeolite;
 - h) milling the product of step (g) for between about 10 minutes and about 15 minutes;
 - i) combining the product of step (f) and the product of step (h) to form a slurry;
 - j) applying said slurry to a substrate; and
 - k) drying and calcining the product of step (j) to form a catalyzed adsorber.
12. The process of Claim 11 wherein an effective amount of promoter is also impregnated on the inorganic-oxide washcoat in step (a)
13. A process for making the catalyzed adsorber of Claim 8 comprising:
- a) impregnating a catalytically effective amount of noble metal reagent on an inorganic oxide washcoat, thereby making a noble-metal-impregnated washcoat;
 - b) drying the noble-metal-impregnated washcoat for at least 24 hours;
 - c) optionally calcining the washcoat at a temperature above about 250°C for between about 1 and about 2 hours;
 - d) preparing an aqueous suspension of the washcoat;
 - e) adjusting the pH of the suspension to between about 3.1 and about 3.9 by the addition of an organic acid;

- f) milling the suspension for about 1 hour, thereby forming a washcoat coating;
- g) preparing an aqueous suspension of zeolite;
- h) milling the product of step (g) for between about 10 minutes and about 15 minutes, thereby forming a zeolite coating;
- 5 i) applying a coating selected from the group consisting of the washcoat coating and the zeolite coating to a substrate;
- j) applying the coating not applied in step (i) on top of the coating applied in step (i); and
- k) drying and calcining the product of step (j) to form a catalyzed adsorber.

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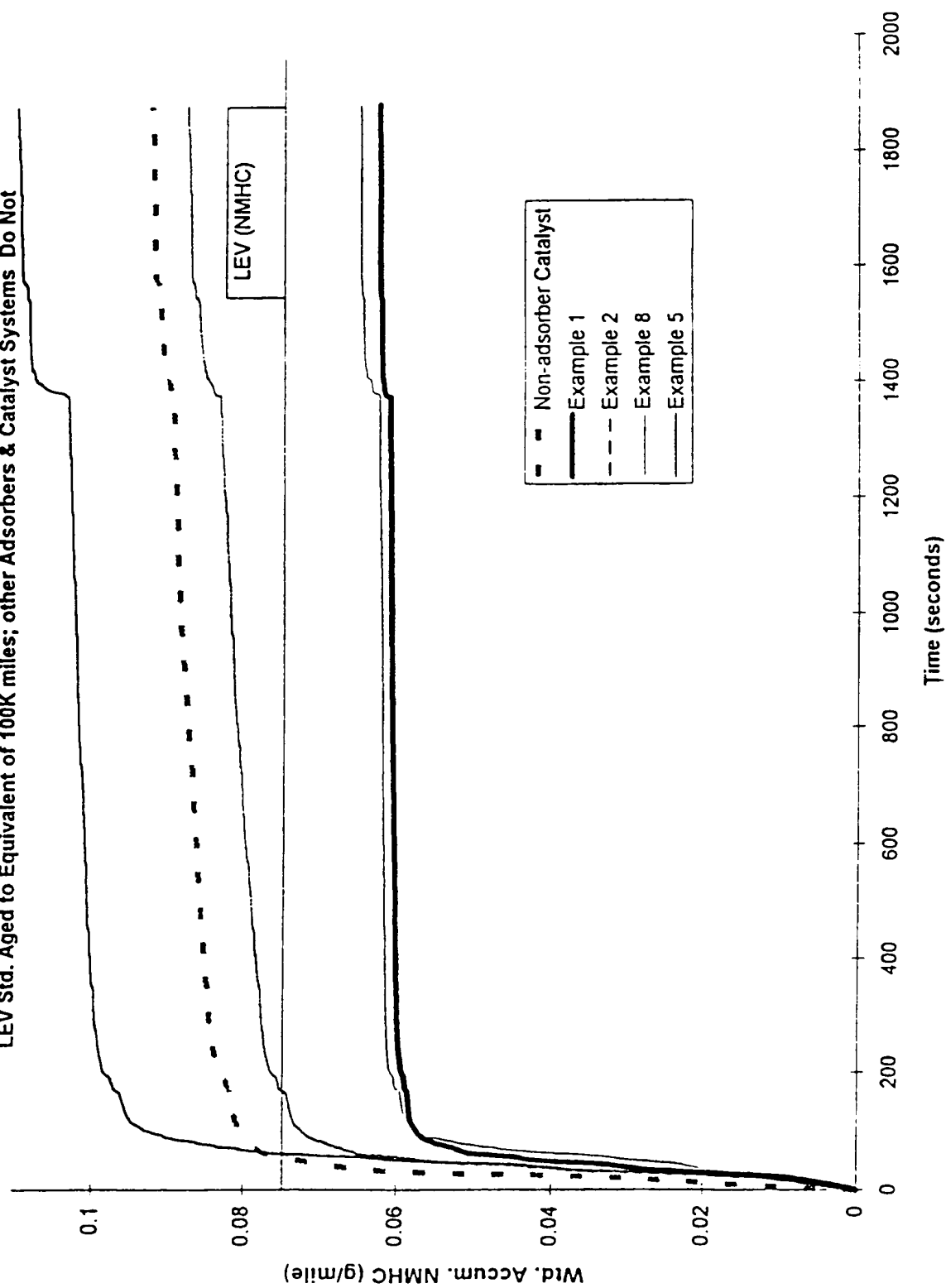
14. The process of Claim 13 wherein an effective amount of promoter is also impregnated on the inorganic-oxide washcoat in step (a).

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15. A catalyzed adsorber for treating motor vehicle exhaust gas comprising a substrate having first dispersed thereon a zeolite layer, said zeolite layer having then dispersed thereon an inorganic-oxide-washcoat layer, said washcoat layer then being impregnated with a catalytically effective amount of noble metal and optionally with a promoter.

Figure 1.

3.8L Olds 88 HC Emissions with PAC System made with Adsorber of Present Invention (Examples 1 & 8) meets LEV Std. Aged to Equivalent of 100K miles; other Adsorbers & Catalyst Systems Do Not



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Figure 2.

Rate of HC Emissions from Converters in Figure 1 Reveals Advantage of Adsorber parts over Non-Adsorber; Present Invention Improved over Previous Art

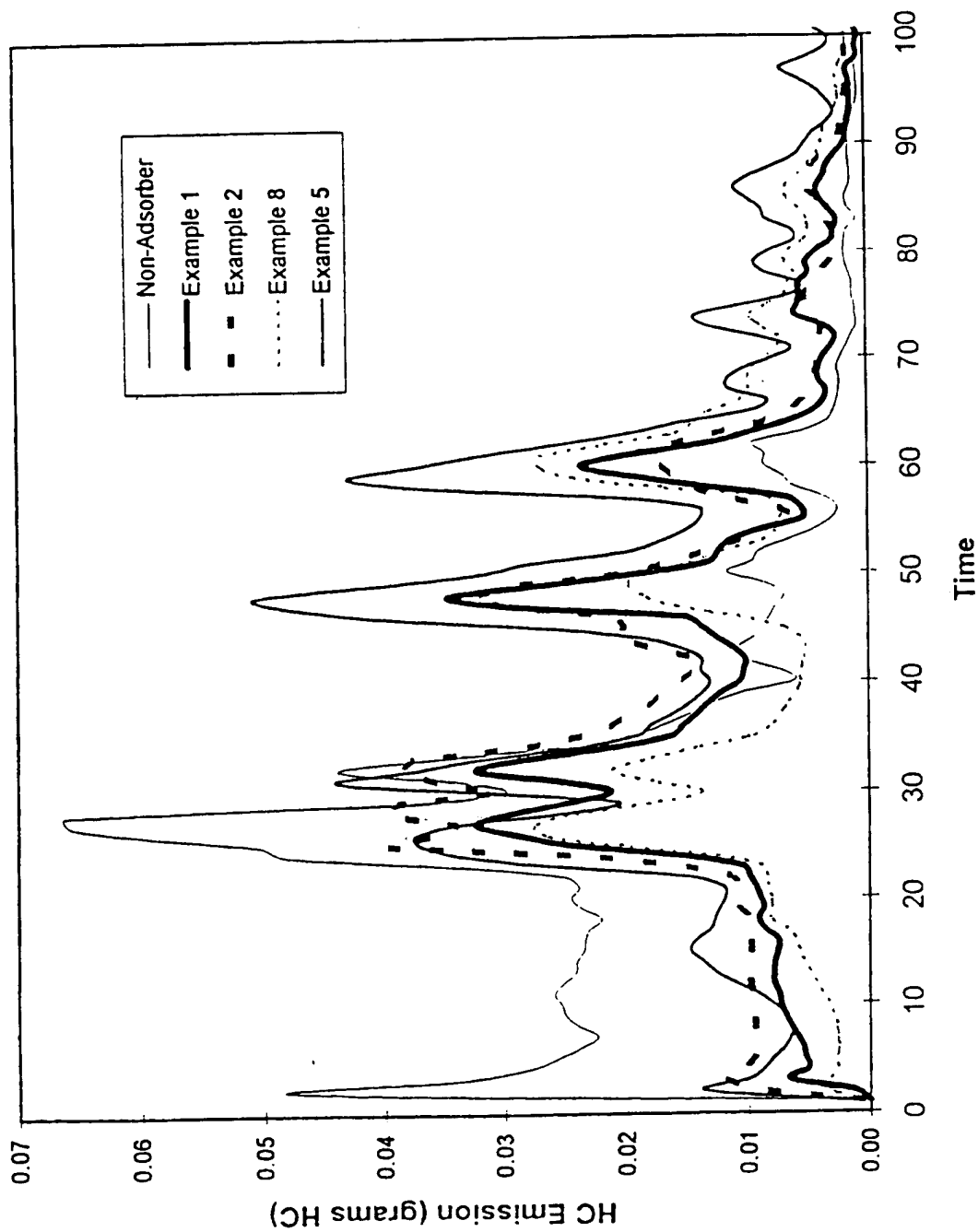


Figure 3. Example 1 vs. Example 6 (Pd vs. Pt) Catalyzed Adsorber Shows Each Has HC Adsorption and Lightoff, but Example 1 is Preferred.

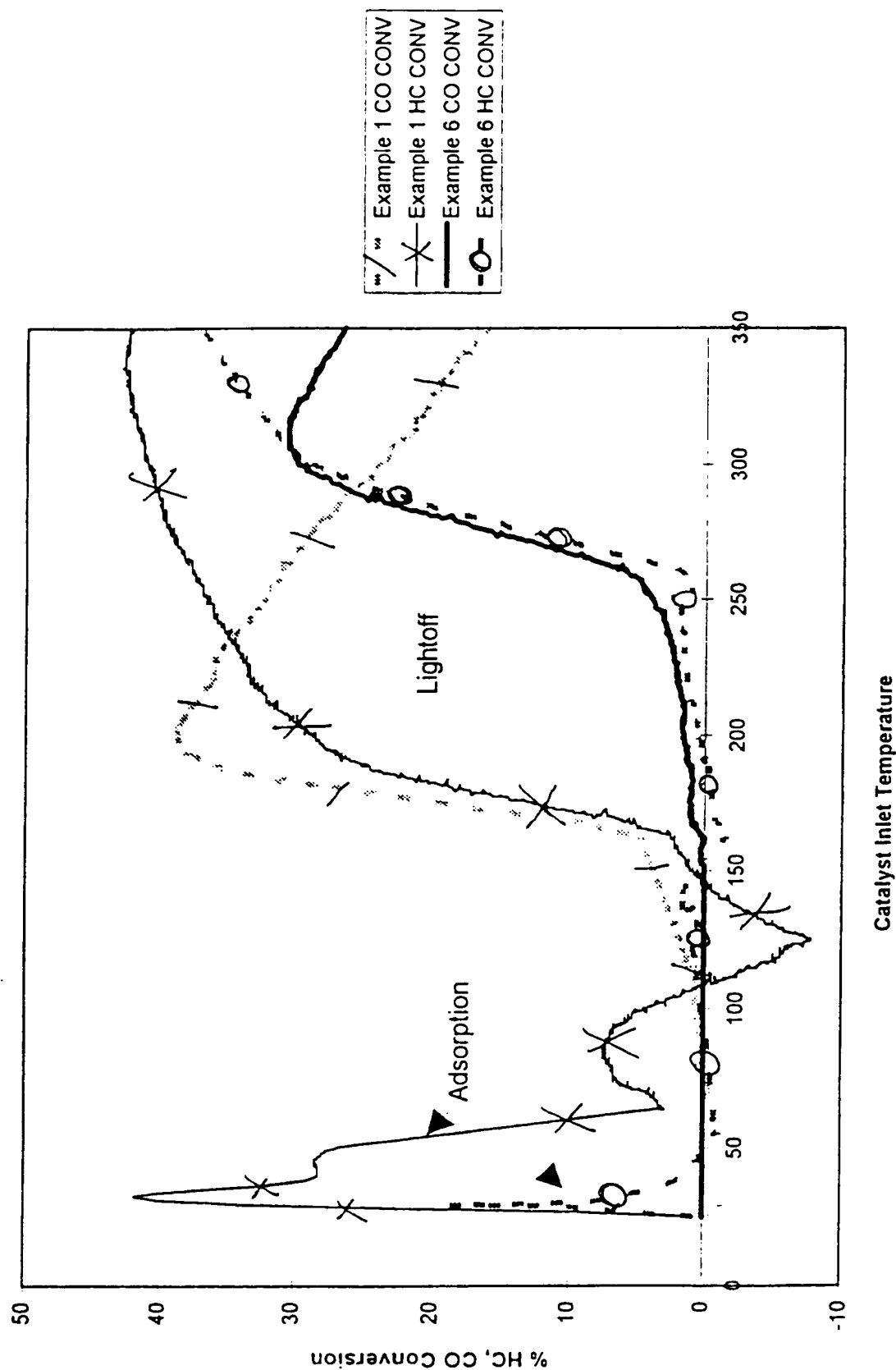


Figure 4. Example 1 vs. Example 7 (Pd vs. Rh) Catalyzed Adsorber Shows
Adsorption and Lightoff on Each Sample

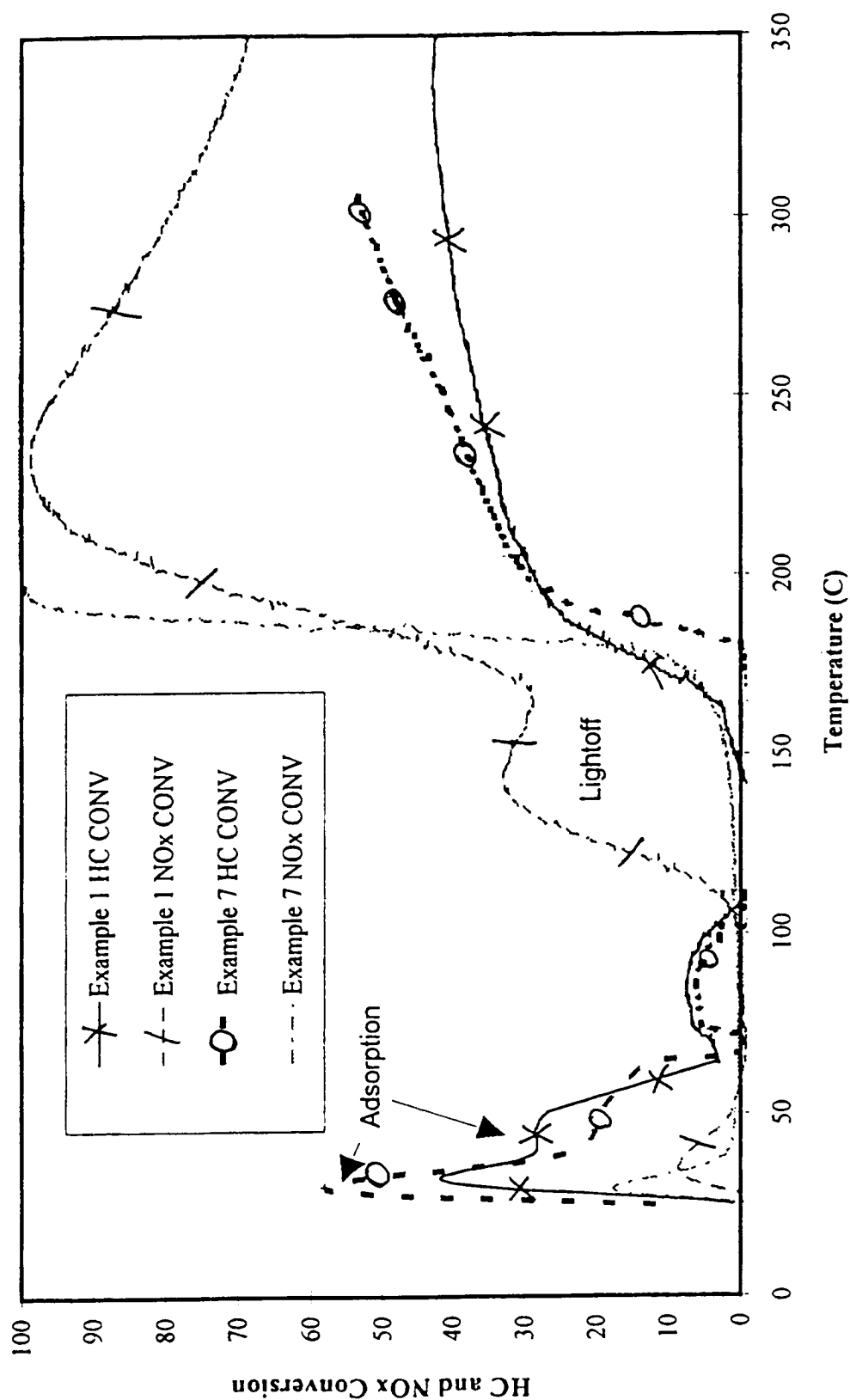


Figure 5.
NM Prevents Loss of Adsorber Capacity

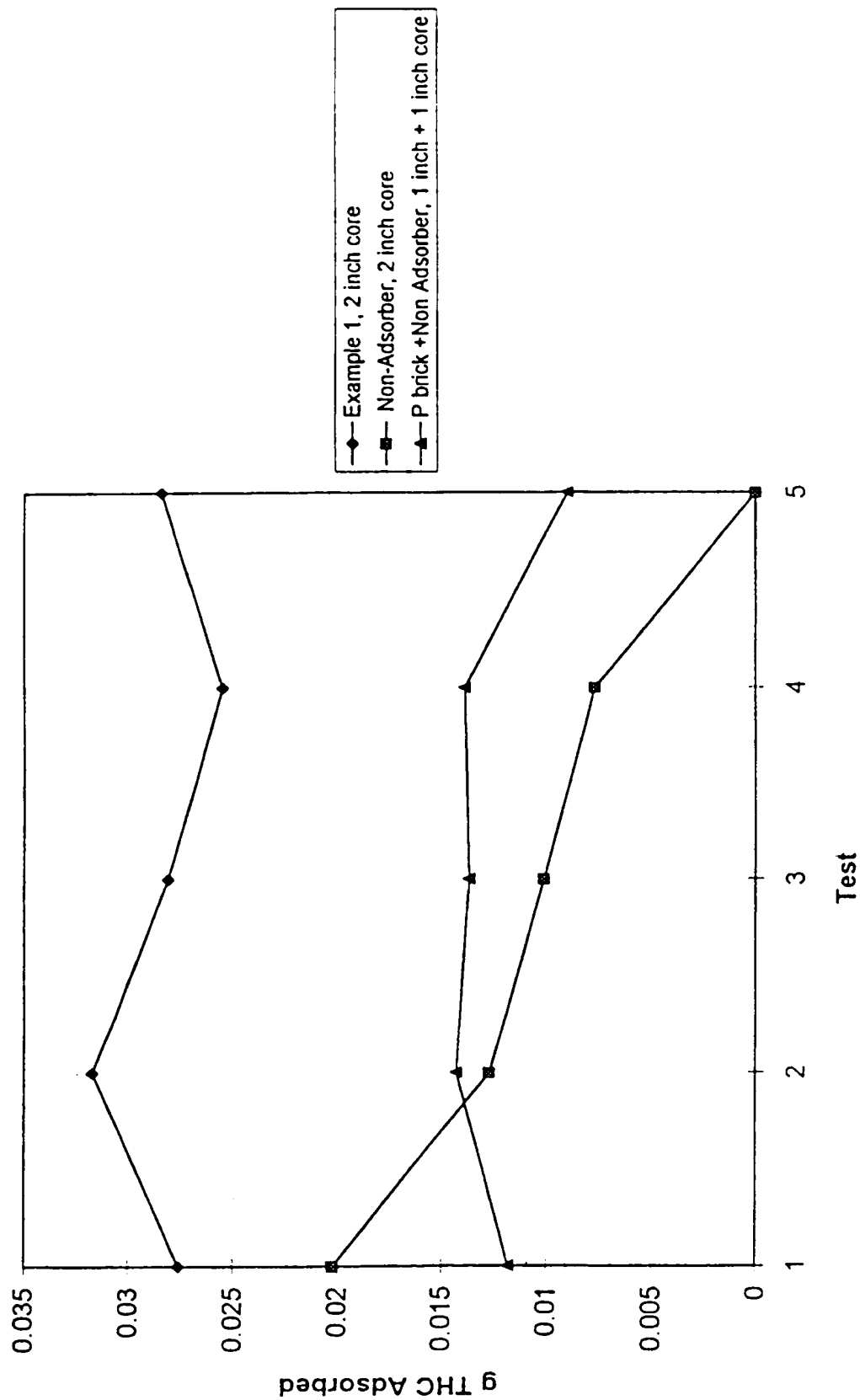
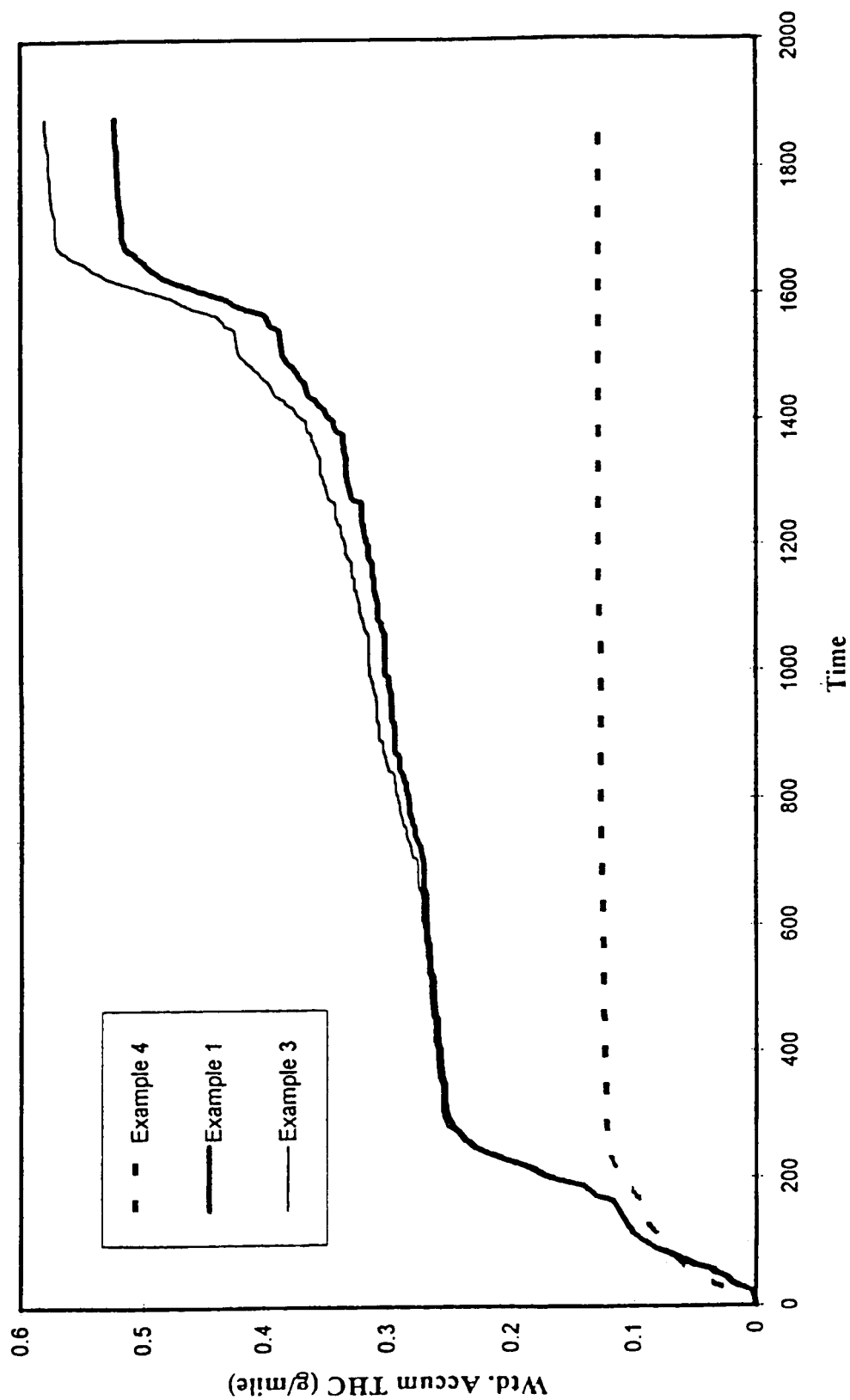


Figure 6.

Results on MB 2.0L with AC system shows Example 4 is improved after High Temperature (970 C Inlet) European Aging over Examples 1 and 3.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/14370

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : BO1J 21/00, 29/06, 31/00; BO1D 50/00

US CL : 502/66, 74, 102, 104; 422/168

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/66, 74, 102, 104; 422/168, 169, 171; 423/212, 213.5, 235

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: inventor name search, zeolite, inorganic oxide, noble metal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X —,P Y	US 5,662,869 A (ABE et al) 02 September 1997, col. 3 - col. 6.	1-5, 8-10, 15 ----- 6, 7
Y	US 5,168,085 A (ADDIEGO et al) 01 December 1992, col. 6, lines 26-30; col. 10, lines 37-39.	6
Y	US 4,711,770 A (SKEELS et al) 08 December 1987, col. 3, lines 26-51; col. 27, lines 55-58.	7
A	US 4,985,210 A (MINAMI) 15 January 1997	1-10, 15
A	US 5,057,244 A (DUNNE et al) 24 September 1991	1-15
A	US 5,078,979 A (DUNNE) 07 January 1992	1-15

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

17 SEPTEMBER 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,447,694 A (SWAROOP et al) 05 September 1995	1-15
A	US 4,882,307 A (TSAO) 21 November 1989	11-14
A	US 5,278,113 A (ONO et al) 11 January 1994	11-14

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